Thermochimica Acta, 123 (1988) 285–291
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDIES ON THERMODYNAMIC PROPERTIES OF BINARY SYSTEMS CONTAINING ALCOHOLS. VII. TEMPERATURE DEPENDENCE OF EXCESS ENTHALPIES FOR n-PROPANOL + BENZENE AND n-BUTANOL + BENZENE *,**

J.P. CHAO and M. DAI

Research Laboratory of Solution Chemistry, Henan Institute of Chemistry, Zhengzhou, Henan (People's Republic of China)

(Received 21 April 1987)

ABSTRACT

Excess enthalpies for binary mixtures of n-propanol with benzene and n-butanol with benzene have been determined at eight temperatures from 288.15 to 323.15 K. It is concluded that excess enthalpies for the latter mixture are larger than for the former at the same temperature; maximal values of these two series shift slightly in the alkanol-rich direction with increasing temperature. Approximately linear relations are found between the excess enthalpies and temperature.

INTRODUCTION

In parts I–III of this series [1–3], the authors systematically investigated molar excess enthalpies of C_1–C_5 normal alcohols with aromatic and heterocyclic compounds at 298.15 K. In order to examine the influence of temperature on excess enthalpies, in this work we have further measured H^E of n-propanol + benzene and n-butanol + benzene at eight temperatures. Additionally, excess heat capacities C_p^E of the two systems were estimated from the temperature dependence of the excess enthalpies at equal mole fractions.

EXPERIMENTAL

Excess enthalpies were measured with a Picker flow microcalorimeter operated in the discontinuous mode. Before taking measurements, the per-

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* Paper presented at the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, Hangzhou, People's Republic of China, 5–7 November 1986.

** Project Supported by Science Fund of the Chinese Academy of Sciences.

TABLE 1

Excess enthalpies H^E for binary systems of n-propanol with benzene at various temperatures; x is the mole fraction of n-propanol

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
$T = 288.15$ K					
0.0757	565.1	0.3612	904.2	0.6682	616.9
0.1129	673.8	0.3951	897.7	0.7138	542.5
0.1496	751.2	0.4286	883.0	0.7587	462.9
0.1859	809.0	0.4617	861.6	0.8028	383.9
0.2218	852.7	0.4945	834.4	0.8463	302.2
0.2573	880.3	0.5268	800.0	0.8891	218.7
0.2923	899.8	0.5748	744.4	0.9312	135.3
0.3270	905.9	0.6218	685.1		
$T = 293.15$ K					
0.0757	602.5	0.3612	977.7	0.6682	669.4
0.1129	722.8	0.3951	971.5	0.7138	589.9
0.1496	808.8	0.4286	958.4	0.7587	502.5
0.1859	868.6	0.4617	934.5	0.8028	417.2
0.2218	914.9	0.4945	906.8	0.8463	332.5
0.2573	947.2	0.5268	869.9	0.8891	241.6
0.2923	966.4	0.5747	808.9	0.9312	145.1
0.3270	976.3	0.6218	743.6		
$T = 298.15$ K					
0.0757	649.9	0.3612	1048.8	0.6682	722.3
0.1129	773.4	0.3951	1042.9	0.7138	631.6
0.1496	862.3	0.4286	1025.4	0.7587	541.7
0.1859	932.1	0.4617	1003.7	0.8028	451.9
0.2218	980.3	0.4945	972.1	0.8463	359.7
0.2573	1017.3	0.5268	940.0	0.8891	261.3
0.2923	1039.7	0.5747	874.8	0.9312	161.3
0.3270	1048.5	0.6218	796.4		
$T = 303.15$ K					
0.0757	676.2	0.3612	1126.6	0.6682	793.7
0.1129	818.5	0.3951	1115.2	0.7138	691.2
0.1496	917.0	0.4286	1100.1	0.7587	597.7
0.1859	992.9	0.4617	1075.7	0.8028	494.0
0.2218	1047.5	0.4945	1045.1	0.8463	397.5
0.2573	1084.0	0.5268	1015.2	0.8891	294.0
0.2923	1111.1	0.5747	953.2	0.9312	178.2
0.3270	1124.1	0.6218	873.2		
$T = 308.15$ K					
0.0757	685.7	0.3612	1203.4	0.6683	859.6
0.1129	834.1	0.3951	1202.5	0.7188	746.6
0.1496	939.7	0.4286	1190.8	0.7587	652.6
0.1859	1028.9	0.4617	1168.0	0.8028	546.9
0.2218	1091.7	0.4945	1135.6	0.8463	440.3
0.2573	1140.3	0.5268	1100.8	0.8891	325.1
0.2923	1173.5	0.5747	1035.7	0.9312	191.4
0.3270	1193.6	0.6218	950.1		

TABLE 1 (continued)

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
$T = 313.15$ K					
0.0757	710.2	0.3612	1276.8	0.6682	937.7
0.1129	880.3	0.3951	1276.1	0.7138	833.7
0.1496	986.6	0.4286	1265.9	0.7587	721.5
0.1859	1082.2	0.4617	1255.7	0.8028	600.1
0.2218	1147.7	0.4945	1219.3	0.8463	473.8
0.2573	1204.2	0.5268	1187.3	0.8891	344.8
0.2923	1238.7	0.5747	1115.9	0.9312	215.3
0.3270	1263.6	0.6218	1030.4		
$T = 318.15$ K					
0.0757	739.9	0.3612	1345.0	0.6682	1016.4
0.1129	899.9	0.3951	1350.8	0.7138	908.4
0.1496	1030.5	0.4286	1345.8	0.7587	787.9
0.1859	1133.0	0.4617	1330.4	0.8028	660.7
0.2218	1207.8	0.4945	1300.5	0.8463	523.9
0.2573	1264.9	0.5268	1265.9	0.8891	386.8
0.2923	1307.9	0.5747	1198.6	0.9312	239.9
0.3270	1335.1	0.6218	1114.0		
$T = 323.15$ K					
0.0757	776.5	0.3612	1426.4	0.6682	1093.0
0.1129	951.1	0.3951	1433.0	0.7138	983.1
0.1496	1087.4	0.4286	1427.6	0.7587	859.2
0.1859	1193.7	0.4617	1410.3	0.8028	721.7
0.2218	1273.4	0.4945	1386.0	0.8463	571.0
0.2573	1336.4	0.5268	1352.2	0.8891	422.6
0.2923	1381.0	0.5747	1282.7	0.9312	263.1
0.3270	1410.3	0.6218	1195.1		

formance of this calorimeter was checked by measuring molar excess enthalpies of benzene–cyclohexane at 298.15 [4], 308.15 [5] and 323.15 K [4]. The agreement with literature values was within 1% at $x = 0.5$.

The n-propanol was obtained from Riedel-de Haen (chromatographic grade) and others from Shanghai Chemical Co. (analytical grade). All reagents were treated prior to use by the methods described in ref. 6. The refractive indices of the pure liquids were in agreement with available literature values. The purified chemicals were partially degassed with a unit similar to that of Bell et al. [11] before being transferred to the microcalorimeter.

RESULTS AND DISCUSSION

Molar excess enthalpies H^E of the systems under investigation have been measured at ordinary pressure and at 288.15, 293.15, 298.15, 303.15, 308.15,

TABLE 2

Excess enthalpies H^E for binary systems of n-butanol with benzene at various temperatures; x is the mole fraction of n-butanol

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
T = 288.15 K					
0.0899	668.7	0.3495	975.4	0.6299	688.1
0.1221	758.0	0.3822	960.0	0.6799	603.9
0.1544	827.2	0.4150	942.9	0.7300	518.7
0.1868	880.1	0.4479	915.5	0.7803	419.0
0.2192	921.8	0.4809	882.3	0.8307	320.8
0.2517	948.0	0.5304	828.5	0.8813	218.9
0.2842	968.6	0.5800	762.9	0.9321	114.2
0.3168	974.5				
T = 293.15 K					
0.0899	722.2	0.3495	1057.9	0.6299	755.5
0.1221	815.3	0.3822	1049.6	0.6799	664.1
0.1544	889.2	0.4150	1032.6	0.7300	567.9
0.1868	949.2	0.4479	1007.0	0.7803	467.4
0.2192	993.7	0.4809	976.6	0.8307	363.4
0.2517	1025.1	0.5303	912.0	0.8813	252.7
0.2842	1045.6	0.5800	840.9	0.9321	141.7
0.3168	1056.8				
T = 298.15 K					
0.0899	767.0	0.3495	1142.0	0.6299	824.9
0.1221	866.6	0.3822	1136.9	0.6799	728.7
0.1544	949.5	0.4150	1120.2	0.7300	624.4
0.1868	1008.0	0.4479	1093.5	0.7803	515.9
0.2192	1060.5	0.4809	1059.8	0.8307	400.9
0.2517	1096.2	0.5304	993.1	0.8813	280.7
0.2842	1120.4	0.5800	916.9	0.9321	162.6
0.3168	1136.2				
T = 303.15 K					
0.0899	809.0	0.3495	1203.0	0.6299	899.8
0.1221	922.1	0.3822	1196.2	0.6799	797.6
0.1544	1003.2	0.4150	1181.2	0.7300	682.0
0.1868	1064.5	0.4479	1158.1	0.7803	557.9
0.2192	1118.6	0.4809	1126.8	0.8307	430.1
0.2517	1158.4	0.5304	1069.2	0.8813	310.2
0.2842	1184.5	0.5801	990.4	0.9321	180.8
0.3168	1201.8				
T = 308.15 K					
0.0899	822.1	0.3495	1273.0	0.6299	965.2
0.1221	946.2	0.3822	1262.3	0.6799	855.1
0.1544	1037.0	0.4150	1249.9	0.7300	735.2
0.1868	1115.3	0.4479	1226.3	0.7803	610.2
0.2192	1172.3	0.4809	1193.7	0.8307	479.9
0.2517	1213.4	0.5304	1127.1	0.8813	340.1
0.2842	1242.5	0.5801	1060.3	0.9321	199.4
0.3168	1262.2				

TABLE 2 (continued)

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
$T = 313.15$ K					
0.0899	851.0	0.3495	1340.2	0.6299	1030.0
0.1221	986.1	0.3822	1337.5	0.6799	913.4
0.1544	1093.1	0.4150	1325.9	0.7300	782.4
0.1868	1168.9	0.4479	1302.9	0.7803	650.3
0.2192	1235.4	0.4809	1272.6	0.8307	507.9
0.2517	1279.9	0.5304	1211.2	0.8813	734.8
0.2842	1310.9	0.5801	1130.1	0.9321	223.0
0.3168	1329.2				
$T = 318.5$ K					
0.0899	895.5	0.3495	1436.7	0.6299	1127.5
0.1221	1044.4	0.3822	1438.2	0.6799	1003.7
0.1544	1154.9	0.4150	1429.7	0.7300	863.7
0.1868	1240.1	0.4479	1406.2	0.7803	721.5
0.2192	1304.8	0.4809	1376.0	0.8307	563.0
0.2517	1358.1	0.5304	1309.0	0.8813	395.5
0.2842	1398.3	0.5801	1229.2	0.9321	235.1
0.3168	1425.4				
$T = 323.15$ K					
0.0899	952.6	0.3495	1530.5	0.6299	1234.2
0.1221	1103.8	0.3822	1533.7	0.6799	1111.6
0.1544	1224.9	0.4150	1525.9	0.7300	962.8
0.1868	1314.9	0.4479	1504.4	0.7803	800.7
0.2192	1392.3	0.4809	1477.7	0.8307	629.5
0.2517	1448.8	0.5304	1422.7	0.8813	444.8
0.2842	1488.4	0.5801	1339.3	0.9321	259.5
0.3168	1516.2				

313.15, 318.15 and 323.15 K. The results obtained are given in Tables 1 and 2. The experimental data were correlated using the Redlick–Kister equation

$$H^E = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \qquad (1)$$

where x is the mole fraction of the alkanol. Values of coefficients A_i were found by the method of least squares and are summarized in Table 3. The standard deviations σ for the excess enthalpies are also given in the last column. The excess enthalpies are plotted as a function of composition at eight temperatures in Figs. 1 and 2. Our H^E values of these two series well agree with those reported by Brown and Fock [7] and Mrazek and Van Ness [8] at 298.15, 308.15 and 318.15 K.

It is evident that H^E values for the mixture of n-butanol with benzene are larger than those for n-propanol with benzene at the same temperature. The

TABLE 3

The coefficients of eqn. (1) and the standard deviations

T (K)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	σ (J mol^{-1})
n-Propanol + benzene									
288.15	3305.9	1811.5	1326.5	1518.4	−1506.7	−2389.6	4335.7	4901.8	2.0
293.15	3597.5	1932.8	1025.8	1587.2	−141.9	−2641.8	3190.0	5367.9	1.9
298.15	3862.4	2023.1	1278.7	2209.9	−1089.5	−4499.1	4533.1	7185.8	2.4
303.15	4172.1	1961.7	1248.2	3133.0	−365.5	−6168.7	3655.3	8054.5	2.1
308.15	4531.3	2046.2	804.4	2703.0	627.4	−6560.8	2659.2	9047.0	2.0
313.15	4858.5	2103.0	1026.0	737.1	−216.1	1077.5	3438.4	2137.6	2.8
318.15	5172.4	1889.4	1446.3	2815.7	−1624.9	−5278.6	4805.7	7257.5	3.4
323.15	5509.0	1916.1	1562.4	2216.9	−1486.5	−3108.1	4676.6	5858.7	3.1
n-Butanol + benzene									
288.15	3450.6	2203.9	1601.3	1467.7	−1877.9	−2315.2	4532.5	5408.4	1.4
293.15	3801.8	2400.1	1289.2	1135.5	1003.6	−1889.0	4464.5	5377.2	2.6
298.15	4136.1	2553.2	1339.5	400.6	−1374.9	331.7	5177.9	3716.3	2.1
303.15	4420.1	2334.8	1428.3	2152.0	−1618.2	−2633.5	5735.6	5491.1	1.4
308.15	4679.1	2436.3	1790.0	1044.8	−2598.9	1123.6	6490.0	1458.6	3.0
313.15	5005.8	2363.5	1101.1	2941.9	185.0	−4193.5	3747.8	5683.7	1.7
318.15	5411.8	2537.0	1331.2	832.7	−497.9	2413.9	4125.9	677.3	1.9
323.15	5829.4	2269.8	1784.6	2878.3	−1671.2	−2616.9	5351.1	5016.2	1.7

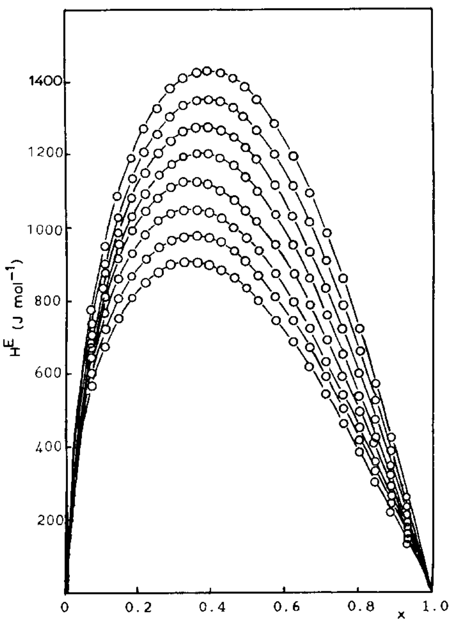
maximal values of these two systems slightly shift in the n-alcohol-rich direction with increasing temperature. Approximately linear relations are found between H^E and temperature. The temperature dependence of excess enthalpies is fitted to the linear expression

$$H^E = a + bT \tag{2}$$

The coefficients a and b were found by the least-squares method. The relevant coefficients for the systems of n-propanol and n-butanol with benzene at $x = 0.5$ are 0.9993 and 0.9975, respectively. According to the definition

$$C_p^E = (\partial H^E / \partial T)_p \tag{3}$$

In this case, C_p^E is a constant for a certain mole fraction. The molar excess heat capacities at eight temperatures and equal molar fraction for these two systems were estimated. For n-propanol + benzene, the excess heat capacity obtained in this work is 15.85 J mol^{-1} K^{-1} and essentially agrees with the values reported by Recko [9] and that calculated from HMW equation [10]. For n-butanol + benzene, the excess heat capacity is 16.41 J mol^{-1} K^{-1}. Until recently no experimental results could be found for comparison, but our C_p^E value is in agreement with that calculated from HMW [10].



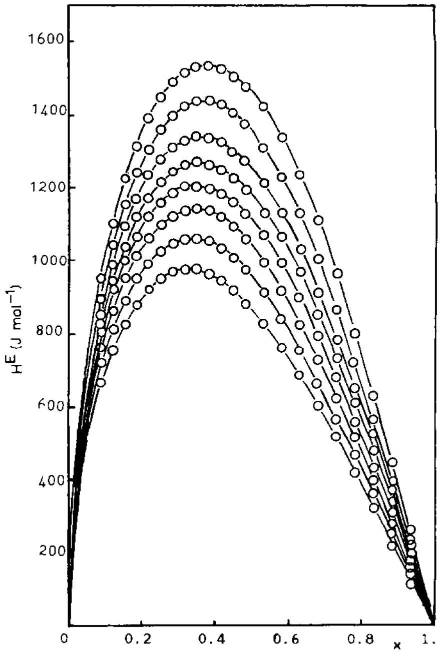


Fig. 1. Excess enthalpies of n-propanol with benzene at various temperatures. Curves, calculated results from eqn. (1) with coefficients from Table 3; circles, experimental data; temperatures, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K (from the lowest curves upwards).

Fig. 2. Excess enthalpies of n-butanol with benzene at various temperatures. Curves, calculated results from eqn. (1) with coefficients from Table 3; circles, experimental data; temperatures, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K (from the lowest curves upwards).

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